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(54) Method of preparing group II metal overbased sulfurized alkylphenols

(57) Group II metal overbased sulfurized alkylphenols are prepared by a step-wise process involving the use of a higher alkyl group-substituted phenol, an oil-soluble Group II metal overbased hydrocarbyl sulfonate, a higher alkanol, a Group II metal oxide, hydroxide or alkoxide, sulfur, an alkylene glycol, carbon dioxide and a sulfurization catalyst. The use of a sulfurization catalyst in this process results in a product generally characterised as having lower crude sediment, a higher Total Base Number and lower viscosity than a similar product prepared without using a sulfurization catalyst.

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SPECIFICATION

Method of preparing group II metal overbased sulfurized alkylphenols

- 5 This invention relates to a method of preparing Group II metal overbased sulfurized alkylphenols. 5
Group II metal overbased sulfurized alkylphenols are useful lubricating oil additives which impart
detergency and dispersancy properties to the lubricating oil composition as well as providing for
an alkalinity reserve in the oil. Alkalinity reserve is necessary in order to neutralize acids
generated during engine operation. Without this alkalinity reserve, the acids so generated would
10 result in harmful engine corrosion. 10
One method of preparing Group II metal overbased sulfurized alkylphenols is described in U.S.
Patent No. 3,178,368, where an alkylphenol, a sulfonate, a high molecular weight alcohol,
lubricating oil and sulfur are combined and heated with agitation. Hydrated lime is then added,
the system heated and ethylene glycol added. Water of reaction is removed, the mixture cooled,
15 and carbon dioxide added. Uncombined CO₂ is removed and the reaction vessel is heated to 15
remove ethylene glycol, water and the high molecular alcohol. The product is overbased by the
incorporation therein of hydrated lime and carbon dioxide.
U.S. Patent No. 3,367,867 discloses a similar process to that of U.S. Patent No. 3,178,368
with the exception that this reference discloses that the use of alkyl groups on the alkylphenol
20 which are mixtures of straight- and branched-chain alkyl results in products having suitable 20
viscosities as well as antifoaming properties.
We have now discovered a novel method for preparing Group II metal overbased sulfurized
alkylphenols. In particular, in the method of the present invention, Group II metal overbased
sulfurized alkylphenols are prepared by employing a "sulfurization catalyst" in the preparation of
25 these additives. 25
To our knowledge, the use of a sulfurization catalyst in the preparation of Group II metal
overbased sulfurized alkylphenols is not taught in the published prior art. Prior art references
include U.S. Patent No. 4,100,085 which describes the use of ammonia or ammonium hydroxide
as a promoter in the synthesis of overbased sulfurized alkylphenols. Likewise, U.S. Patent No.
30 4,212,752 describes the use of certain amino promoters, such as primary and secondary 30
alkylamines, polyalkyleneamines, amino acids, etc., in the synthesis of overbased sulfurized
alkylphenols.
According to the invention, there is provided a method of preparing a Group II metal over-
based sulfurized alkylphenol which comprises the steps of:
35 (a) introducing into an inert hydrocarbon diluent an alkylphenol in which the alkyl group 35
contains a sufficient number of carbon atoms to render oil-soluble the resulting Group II metal
overbased sulfurized alkylphenol, an oil-soluble Group II metal overbased natural or synthetic
hydrocarbyl sulfonate, a sulfurization catalyst, and a higher alkanol of at least 8 carbon atoms;
the oil-soluble Group II metal overbased natural or synthetic hydrocarbyl sulfonate being em-
40 ployed at from 1 to 20 weight percent to the alkylphenol; the sulfurization catalyst being 40
employed at from 0.5 to 10 weight percent to the alkylphenol, and the higher alkanol being
employed at a molar ratio to the alkylphenol of from 0.5 to 5;
(b) heating the resulting reaction system to a temperature of from 90°C to 115°C;
(c) introducing into the reaction system a Group II metal oxide, hydroxide or C₁-C₆ alkoxide
45 and sulfur at a temperature sufficient to effect sulfurization of the alkylphenol followed by 45
addition at from 145°C to 165°C of a C₂-C₄ alkylene glycol; the Group II metal oxide, hydroxide
or C₁-C₆ alkoxide being employed at a molar ratio to the alkylphenol of from 1 to 4, the sulfur
being employed at a molar ratio to the alkylphenol of from 1.5 to 4, and the C₂-C₄ alkylene
glycol being employed at a molar ratio to the alkylphenol of from 1 to 4;
50 (d) heating the resulting reaction system at a temperature sufficient to effect removal of a 50
portion of the water in the system;
(e) heating the system to a temperature of from 160°C to 190°C;
(f) introducing into the reaction system carbon dioxide, the carbon dioxide being employed at a
molar charge to the alkylphenol of from 1 to 3; and
55 (g) heating the system under reduced pressure at a temperature and pressure sufficient to 55
remove from the system a portion of the water, C₂-C₄ alkylene glycol and the alkanol of at least
8 carbon atoms, and any unreacted carbon dioxide, and thereafter recovering the required Group
II metal overbased sulfurized alkylphenol from the reaction system.
In step (c), after combination of the Group II metal oxide, hydroxide or C₁-C₆ alkoxide and
60 sulfur, the temperature of the system is preferably raised, if necessary, from that of step (b) to 60
about 150°C to effect sulfurization of the alkylphenol. Also, in step (c), the C₂-C₄ alkylene glycol
addition is preferably conducted at from about 150°C to about 165°C and even more preferably
at from 150°C to 160°C.
Step (d) is preferably conducted at a temperature sufficient to effect removal of a portion of
65 the water in the reaction system without additionally removing significant amounts, i.e., greater 65

than about 15%, of either the alkanol of at least 8 carbon atoms and the C₂-C₄ alkylene glycol. Step (d) is more preferably conducted at from about 155°C to about 165°C and most preferably at about 160°C.

Step (e) is preferably conducted at from about 160°C to about 180°C.

- 5 Step (g) is preferably conducted at from about 175°C to about 200°C and at pressures from about 10 to about 50 mm of mercury. 5

- 10 The alkyl group of the alkylphenol employed in the method of the instant invention contains a sufficient number of carbon atoms to render the Group II metal overbased sulfurized alkylphenol oil-soluble. In general, alkyl groups of about 8 carbon atoms or more are sufficient to render the Group II metal overbased sulfurized alkylphenol oil-soluble. 10

- 15 In one preferred embodiment, the alkyl group of said alkylphenol contains from 25 to 100 mole percent predominantly straight-chain alkyl groups of from 15 to 35 carbon atoms and from 75 to 0 mole percent of the alkyl groups are polypropenyl of from 9 to 18 carbon atoms. More preferably, the alkyl group of said alkylphenol contains from 35 to 100 mole percent predominantly straight-chain alkyl groups of from 15 to 35 carbon atoms and from 65 to 0 mole percent of the alkyl groups are polypropenyl of from 9 to 18 carbon atoms. In yet another preferred embodiment, the alkyl group of said alkylphenol contains from 40 to 70 mole percent predominantly straight-chain alkyl groups of from 15 to 35 carbon atoms and from 60 to 30 mole percent of the alkyl groups are polypropenyl of from 9 to 18 carbon atoms. Most preferably, the alkyl group of said alkylphenol contains approximately 50 mole percent predominantly straight-chain alkyl groups of from 15 to 35 carbon atoms and approximately 50 mole percent of the alkyl groups are polypropenyl of from 9 to 18 carbon atoms. 15 20

- 25 The process of the present invention is particularly but not exclusively useful for preparing highly overbased sulfurized alkylphenols possessing a Total Base Number of greater than about 300; and preferably from about 300 to 400, more preferably from 315 to 400; even more preferably from 315 to 360; and most preferably 325 to 360. 25

- 30 As used herein, the term "Group II metal" means a metal selected from calcium, barium, magnesium, and strontium. Preferably, the Group II metal is selected from the group consisting of calcium, magnesium, barium, and mixtures thereof. Most preferably, the Group II metal is calcium. 30

As used herein, the term "Total Base Number" or "TBN" refers to the amount of base equivalent to milligrams of KOH in 1 gram of sample. Thus, higher TBN numbers reflect more alkaline products and therefore a greater alkalinity reserve.

- 35 The term "hydrolytically stable" as used in conjunction with Group II metal overbased sulfurized alkylphenols means that compositions containing these products will lose less than about 25% of their Total Base Number in a modified ASTM D 2619 test. This test, as modified, measures the hydrolytic stability of a product by measuring its base loss upon exposure to moisture. Greater base loss reflects poorer hydrolytic stability. Hydrolytic stability of the Group II metal overbased sulfurized alkylphenols is an extremely important property particularly in marine crankcase use where water exposure is common. See van der Horst, Lubricant Engineering, "Development of Modern Lubricants for Medium-Speed Marine Diesel Engines" (1977); Thomas et al., "Modern Marine Diesel Engine Lubricants and their Development", Second International Lubricant Symposium, Cairo, Egypt (1979). 35 40

- 45 In the process of preparing overbases sulfurized alkylphenols, only the Group II metal sulfurized alkylphenol is capable of being overbased. Accordingly, it is desirable to maximize the amount of Group II metal sulfurized alkylphenol in the reaction process. On the other hand, unsulfurized alkylphenol can form a Group II metal salt but this salt cannot be overbased by addition of Ca(OH)₂ (and related materials) and carbon dioxide. Accordingly, it is desirable to minimize the amount of Group II metal unsulfurized alkylphenol in the reaction process. 45

- 50 The term "actives" as applied to the compositions of this invention refers to the Group II metal alkylphenol and the Group II metal sulfurized alkylphenol whereas the term "inactives" refers to unreacted alkylphenol as well as any diluent oil contained in the composition. 50

As used herein, the term "predominantly straight chain alkyl" means a predominantly linear alkyl group which may contain some branching in the molecular structure.

- 55 In the method of this invention, the Group II metal overbased sulfurized alkylphenols are prepared in processes similar to those previously described in the art with the exception that a sulfurization catalyst is also employed. Use of a sulfurization catalyst in the process of this invention results in products generally characterized as having lower crude sediment, higher Total Base Numbers (TBN), and lower viscosities than products prepared by the same process but without use of the sulfurization catalyst. 55 60

- 65 The method of the instant invention is generally but not exclusively useful for preparing 300+ TBN products of acceptable viscosity which are also hydrolytically stable. Prior art processes for preparing Group II metal overbased sulfurized alkylphenols can provide products having a Total Base Number as high as 300 or more, some of which have acceptable viscosities but some of these products are hydrolytically unstable. The reasons for the inability of prior art processes to 65

consistently produce hydrolytically stable high TBN overbased sulfurized alkylphenols are not readily apparent.

Upon careful examination of this problem and without limitation to this theory, it appears that the hydrolytic instability of high TBN products is due in part to large amounts of unsulfurized Group II metal alkylphenol contained in the actives. It appears that this incomplete sulfur incorporation is much more prevalent when high molar charges of hydrated lime to alkylphenol are used, i.e., greater than 2. That is to say, in the process of preparing an overbased sulfurized alkylphenol, hydrated lime, sulfur and alkylphenol are charged into a reaction system. Sufficient sulfur is employed to convert all of the alkylphenol to sulfurized alkylphenol. At a molar charge of 2 or less of hydrated lime to alkylphenol, the alkylphenol is generally converted to calcium sulfurized alkylphenol whereas at molar charges of greater than 2, the product contains large amounts of unsulfurized calcium alkylphenol. On the other hand, molar charges of hydrated lime to alkylphenol of greater than 2 are generally required to achieve 300+ TBN products. Thus, the problem is readily apparent. With all other factors held constant such as sulfur charge, CO₂ charge, etc., to arrive at 300+ TBN products requires molar charges of hydrated lime to alkylphenol in excess of 2 which invariably results in large amounts of unsulfurized calcium alkylphenol which in turn reduces the TBN incorporation because it cannot be overbased and tends to increase the viscosity as well as the hydrolytic instability of the product. The incomplete sulfurization of the alkylphenol at high molar charges of hydrated lime to alkylphenol, i.e., >2, was heretofore unrecognized and for which an explanation is not readily available.

In any event, we have now discovered that the use of a sulfurization catalyst in those processes employing greater than 2 equivalents of hydrated lime or other Group II metal oxide or hydroxide greatly enhances the amount of Group II metal sulfurized alkylphenol in the actives and greatly decreases the amount of unsulfurized Group II metal alkylphenol in the actives. The resulting high TBN products are characterized by containing at least about 90 mole percent and preferably at least 95 mole percent of Group II metal sulfurized alkylphenols in the actives. In the converse, these products by necessity will contain at most about 10 mole percent and preferably at most about 5 mole percent of the unsulfurized Group II metal alkylphenols in the actives. Because of the decrease in the amount of unsulfurized Group II metal alkylphenol in the actives, higher TBN products are possible. Moreover by employing a sulfurization catalyst, the resulting products additionally have improved hydrolytic stability, lower viscosity, as well as less crude sediment than products produced without a sulfurization catalyst.

The sulfurization catalyst catalyzes the sulfur incorporation onto the alkylphenol. Suitable sulfurization catalysts include 2-mercaptobenzothiazole (MBT) and derivatives thereof such as bis(2,2'-benzothiazolyl) disulfide; 2(3H)-benzothiazolethione zinc salt; 2-benzothiazolyl-N,N'-diethylthiocarbonyl sulfide; 4-morpholinyl-2-benzothiazole disulfide; etc. Another particularly suitable class of sulfurization catalysts comprises zinc dihydrocarbyl dithiophosphates wherein each hydrocarbyl is independently selected such that the dihydrocarbyl group contains from 6 to 30 carbon atoms, e.g. zinc di-(2-ethylhexyl)dithiophosphate. Hydrocarbyl as used in zinc dihydrocarbyl dithiophosphate means an organic radical composed only of carbon and hydrogen and includes alkyl, aryl, alkaryl, aralkyl, etc. Other metals such as copper, barium, magnesium, etc., are considered equivalent to zinc in the zinc dihydrocarbyl dithiophosphates used as sulfurization catalysts.

Other suitable classes of sulfurization catalysts include thioureas, thiurams and calcium polysulfide. Specific embodiments of these catalysts include N,N'-dibutylthiourea; ethylenethiourea; trimethylthiourea, dipentamethylenethiuram disulfide, dipentamethylenethiourea tetrasulfide; dipentamethylenethiourea hexasulfide; etc.

The sulfurization catalyst is employed at from 0.5 to 10 weight percent to the alkylphenol in the reaction system and preferably at from 1 to 2 weight percent. In a preferred embodiment, the sulfurization catalyst is added to the reaction mixture as a liquid. This can be accomplished by dissolving the sulfurization catalyst in molten sulfur or in the alkylphenol as a premix to the reaction.

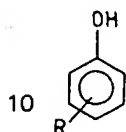
Sulfur is employed at from 1.5 to 4 moles per mole of the alkylphenol in the reaction system; preferably at from 2 to 4 moles per mole of the alkylphenol and even more preferably at from 2 to 3 moles per mole of alkylphenol. All allotropic forms of sulfur can be used. Alternatively, in place of sulfur, sulfur monochloride may be employed. For the purposes of this invention, sulfur monochloride is considered equivalent to sulfur. The sulfur may be employed either as molten sulfur or as a solid.

The Group II metal oxide, hydroxide or C₁-C₆ alkoxide used to prepare the Group II metal alkylphenol includes the oxides, hydroxides and alkoxides of calcium, strontium, barium or magnesium, for example Dolomite (Ca(OH)₂.Mg(OH)₂). However, calcium, barium and magnesium are preferred whereas calcium is most preferred. The Group II metal oxide, hydroxide, or C₁-C₆ alkoxide is employed at a molar charge to the alkylphenol of from 1 to 4; although preferably at from greater than 2 to 4; and even more preferably from greater than 2 to 3.

Carbon dioxide is added to the reaction system in conjunction with the Group II metal oxide, hydroxide or C₁-C₆ alkoxide to form overbased products and is employed from 1 to 3 moles per

mole of alkylphenol, although preferably from about 2 to 3 moles per mole of alkylphenol charged to the reaction system. Preferably, the amount of CO₂ incorporated into the Group II metal overbased sulfurized alkylphenol is such that the CO₂ to calcium weight ratio is between 0.65 to 0.73.

5 The alkylphenol employed in this invention is represented by the formula:



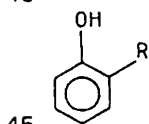
I

wherein R is an alkyl group containing sufficient number of carbon atoms to render the resulting Group II metal overbased sulfurized alkylphenol oil-soluble.

15 Preferably, R is alkyl wherein from about 25 to 100 mole percent of the alkyl group is predominantly straight-chain alkyl of from 15 to 35 carbon atoms and from about 75 to 0 mole percent of the alkyl group is polypropenyl of from 9 to 18 carbon atoms although more preferably R is alkyl wherein from about 35 to 100 mole percent of the alkyl group is predominantly straight chain of from 15 to 35 carbon atoms and from about 65 to 0 mole percent of the alkyl group is polypropenyl of from 9 to 18 carbon atoms. Use of increasing amounts of predominantly straight chain alkyl results in high TBN products generally characterized by lower viscosities. On the other hand, while polypropenylphenols are generally more economical than predominantly straight chain alkylphenols, use of greater than 75 mole percent polypropenylphenol in the preparation of Group II metal overbased sulfurized alkylphenol generally results in products of unacceptably high viscosities. However, use of a mixture of from 75 mole percent or less of polypropenylphenol of from 9 to 18 carbon atoms and from 25 mole percent or more of predominantly straight chain alkylphenol of from 15 to 35 carbon atoms allows for more economical products of acceptable viscosities.

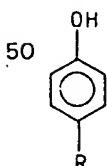
20 The alkylphenols of Formula I above are prepared by reacting the appropriate olefin or olefin mixture with phenol in the presence of an alkylating catalyst at a temperature of from 60°C to 200°C, and preferably 125°C to 180°C either neat or in an essentially inert solvent at atmospheric pressure. A preferred alkylating catalyst is a sulfonic acid catalyst such as Amberlyst 15® available from Rohm and Haas, Philadelphia, Pennsylvania. Molar ratio of reactants may be used. Alternatively, molar excess of phenol can be employed, i.e., 2-2.5 equivalents of phenol for each equivalent of olefin with unreacted phenol recycled. The latter process maximizes monoalkylphenol. Examples of inert solvents include benzene, toluene, chlorobenzene and 250 thinner which is a mixture of aromatics, paraffins and naphthenes.

The alkylphenols employed in this invention are generally either ortho alkylphenols of the formula:



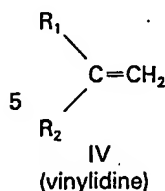
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or para-alkylphenols of the formula:



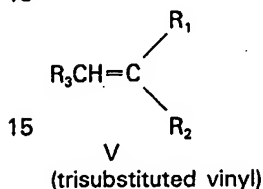
III

50 Preferably, R is predominantly para with no more than about 50 mole percent of the R alkyl group being in the ortho position; and more preferably no more than about 35 mole percent of the alkyl group being in the ortho position. It is believed that p-alkylphenols, III, facilitate the preparation of highly overbased Group II metal sulfurized alkylphenols. Accordingly, it is desirable to employ an olefin which results in maximum para alkylphenol content in the alkylphenol. In this regard, while polypropene generally adds in the para position, olefins containing no branching will add at both the ortho or para position. One method of enhancing the para content of the alkylphenol prepared from straight chain olefins is by use of a predominantly straight chain olefin fractions containing some branching in the molecular structure at the double bond such as structures IV and V



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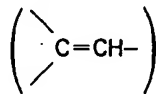
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wherein R_1 , R_2 and R_3 form the remainder of the olefin. While being predominantly straight chain, the branched portion of the molecular structure allows for formation of a tertiary carbonium ion during the alkylation process. Without being limited to any theory, it is believed that the steric hindrance associated with a tertiary carbonium ion inhibits ortho alkylation and thereby results in enhanced para substitution. Suitable predominantly straight chain olefins are those wherein about 75 to 100 number percent and preferably about 85 to 100 number percent of the individual carbon atoms of the olefin are either primary (CH_3-) or secondary ($-CH_2-$). Included in the terms primary or secondary are alpha olefins ($-CH=CH_2$) and internal olefins ($-CH=CH-$). In the converse, such predominantly straight chain olefins can contain from 0 to about 25 number percent although preferably from 0 to about 15 number percent of tertiary carbon atoms. Included within the term tertiary are trisubstituted vinyl groups

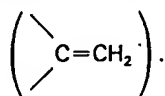
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35 and vinylidene

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Predominantly straight chain olefin fractions are commercially available products such as C_{18} - C_{30} olefins, available from Ethyl Corporation, Baton Rouge, Louisiana. These olefins are predominantly straight chain in that from 80 to 100 number percent of the carbon atoms in the olefins are either primary or secondary. On the other hand, about 40 mole percent of the olefins contained in the olefin fraction are branched olefins. That is to say while being otherwise predominantly straight chain 40 mole percent of all of the olefins are branched in the form of trisubstituted vinyl or vinylidene structure. Likewise, C_{24} - C_{28} olefin fractions, available from Chevron Chemical Corporation, San Francisco, CA, are also predominantly straight-chain but contain about 40 mole percent or more branched olefin, containing predominantly vinylidene olefin. Straight chain olefins, containing less than about 5 mole percent branched olefins, are available from Shell Chemical Company, Houston, Texas.

This is the appropriate time to distinguish between "predominantly straight-chain olefins containing 80 to 100 number percent of either primary or secondary carbon atoms in the olefin" and a "predominantly straight-chain olefin fraction wherein about 40 mole percent of the olefins are branched". In the first case, the olefin is viewed on a molecular basis and requires that at least 80 number percent of the carbon atoms be primary or secondary. In this case, a branched olefin such as trisubstituted vinyl or vinylidene is nonetheless predominantly straight-chain if a sufficient number of the remaining carbon atoms are primary or secondary such that at least 80 number percent of the carbon atoms in this olefin are primary or secondary.

On the other hand, a predominantly straight-chain olefin fraction wherein about 40 mole percent of the olefins are branched as is viewed from a composition basis. That is the predominantly straight-chain olefin fraction can contain olefins such as alpha olefins, internal olefins, trisubstituted vinyl and vinylidene. When viewing the entire predominantly straight-chain olefin fraction, 40 mole percent of the olefins are branched, i.e., either trisubstituted vinyl or vinylidene, whereas the remainder are either alpha olefins or internal olefins.

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The reaction to prepare the Group II metal overbased sulfurized alkylphenols of this invention also employs a C₂-C₄ alkylene glycol, preferably ethylene glycol, a high molecular weight alcohol (generally decyl alcohol) and a Group II metal overbased natural or synthetic hydrocarbyl sulfonate.

5 The C₂-C₄ alkylene glycol is employed at a molar charge to the alkylphenol of 1 to 4, although 5 preferably this molar charge is from 2 to 3. Alternatively, 2-ethylhexanol may be employed in conjunction with C₂-C₄ alkylene glycol at weight ratios such as 80% by weight 2-ethylhexanol and 20% by weight ethylene glycol.

10 The high molecular weight alcohol, i.e., an alkanol of at least 8 carbon atoms, is employed at 10 a molar charge to the alkylphenol from 0.5 to 5, although preferably from about 0.5 to 4 and even more preferably from 1 to 2. Suitable alkanols of at least 8 carbon atoms include 1-octanol, 1-decanol, i.e., decyl alcohol, 2-ethylhexanol, etc.

15 The Group II metal overbased natural or synthetic hydrocarbyl sulfonates may be either 15 petroleum sulfonate, synthetically alkylated aromatic sulfonates, or aliphatic sulfonates such as those derived from polyisobutylene. These sulfonates are well-known in the art. The hydrocarbyl group must have a sufficient number of carbon atoms to render the sulfonate molecule oil soluble. Preferably, the hydrocarbyl portion has at least 20 carbon atoms and may be aromatic or aliphatic, but is usually alkylaromatic. Most preferred for use are calcium, magnesium or barium sulfonates which are aromatic in character.

20 Certain sulfonates are typically prepared by sulfonating a petroleum fraction having aromatic 20 groups, usually mono- or dialkylbenzene groups, and then forming the metal salt of the sulfonic acid material. Other feedstocks used for preparing these sulfonates include synthetically alkylated benzenes and aliphatic hydrocarbons prepared by polymerizing a mono- or diolefin, for example, a polyisobutenyl group prepared by polymerizing isobutene. The metallic salts are formed directly 25 or by metathesis using well-known procedures. 25

The sulfonates are then overbased to yield products having Total Base Numbers up to about 400 or more by addition of carbon dioxide and a Group II metal hydroxide or oxide. Calcium hydroxide or oxide is the most commonly used material to produce the basic overbased sulfonates. Also included in the term "overbased" sulfonates are the basic natural or synthetic 30 hydrocarbyl sulfonates prepared by utilizing an excess of Group II metal oxide or hydroxide over 30 that which is necessary to form the neutral salts. All of these materials are well-known in the art.

The Group II metal overbased natural or synthetic hydrocarbyl sulfonate is employed at from about 1 to 20 weight percent to the alkylphenol, although preferably from about 1 to 10 weight 35 percent. The Group II metal overbased natural or synthetic hydrocarbyl sulfonate described above 35 are also employed in lubricating oil formulations in conjunction with the Group II metal overbased sulfurized alkylphenols; especially in marine crankcase formulations.

The inert hydrocarbon diluent employed in the method of this invention is generally a lubricating oil. Suitable lubricating oil diluents include solvent refined 100N, i.e., Cit-Con 100N, and 40 hydrotreated 100N, i.e., RLOP 100N, etc. 40

Step (d) involves removal of a portion of the water from the system. In this step, water is generally removed from the system until approximately 50% of the water is removed and preferably 80% to 90% or more of the water is removed from the system.

Step (g) involves heating the system under reduced pressures at a temperature and pressure 45 sufficient to remove from the system a portion of the water, C₂-C₄ alkylene glycol and the 45 alkanol of at least 8 carbon atoms. It is understood by those skilled in the art that the temperature required to remove a portion of the water, C₂-C₄ alkylene glycol and the alkanol of at least 8 carbon atoms, and any unreacted carbon dioxide is a function of pressure. That is 50 lower temperatures require lower pressures to effect removal from the system of a portion of 50 water, C₂-C₄ alkylene glycol and the alkanol of at least 8 carbon atoms. All that is required is a sufficiently high temperature and a sufficiently low pressure to effect removal. In general, temperatures of from greater than about 175°C to about 200°C and pressures from about 10 to about 50 mm of mercury or less have been found sufficient. Step (g) is generally continued until approximately all of the water, about 75% to about 90% of the C₂-C₄ alkylene glycol, and about 55 75% to about 90% of the alkanol of at least 8 carbon atoms are removed. Preferably, step (g) 55 is continued until no additional C₂-C₄ alkylene glycol and/or alkanol of at least 8 carbon atoms is removed, i.e., distills in the overhead condenser.

In a preferred embodiment, it has been found that the addition of a demulsifier such as Triton X-45 and Triton X-100 may synergistically enhance the hydrolytic stability of the Group II metal 60 overbased sulfurized alkylphenol. Triton X-45 and Triton X-100 are nonionic detergents useful as 60 demulsifiers and are available from Rohm and Haas, Philadelphia, PA. These demulsifiers are ethoxylated p-octylphenols. Other suitable demulsifiers include Igepal CO-610 available from GAF Corporation, New York, NY. In one preferred embodiment, the demulsifier and sulfurization catalyst are combined. That is the aqueous solution contains calcium polysulfide and Triton X- 65 100. Such a product is sold by Chevron Chemical Company, San Francisco, CA, under the trade 65

name of ORTHORIX®. Demulsifiers are generally added at from 0.1 to 1 weight percent to the alkylphenol, preferably at from 0.1 to 0.5 weight percent.

The oil-soluble, Group II metal overbased sulfurized alkylphenols produced by the process of this invention are useful lubricating oil additives imparting detergency and dispersancy properties to the lubricating oil as well as providing an alkalinity reserve in the oil. When employed in this manner, the amount of the oil-soluble, Group II metal overbased sulfurized alkylphenol ranges from about 0.5 to 40 weight percent of the total lubricant composition although preferably from about 1 to 25 weight percent of the total lubricant composition. Such lubricating oil compositions are useful in diesel engines, gasoline engines as well as in marine engines. When employed in marine engines, the oil-soluble, Group II metal overbased sulfurized alkylphenols are often used in conjunction with an oil-soluble, Group II metal overbased natural or synthetic hydrocarbyl sulfonate.

Such lubricating oil compositions employ a finished lubricating oil which may be single or multigrade. Multigrade lubricating oils are prepared by adding viscosity index (VI) improvers. Typical viscosity index improvers are polyalkyl methacrylates, ethylene, propylene copolymers, styrene-diene copolymers, and the like. So-called decorated VI improvers having both viscosity index and dispersant properties are also suitable for use in the formulations of this invention.

The lubricating oil used in such compositions may be mineral oil or synthetic oils of viscosity suitable for use in the crankcase of an internal combustion engine such as gasoline engines and diesel engines which include marine engines. Crankcase lubricating oils ordinarily have a viscosity of about 1300 cSt 0°F to 24 cSt at 210°F (99°C). The lubricating oils may be derived from synthetic or natural sources. Mineral oil for use as the base oil in this invention includes paraffinic, naphthenic and other oils that are ordinarily used in lubricating oil compositions. Synthetic oils include both hydrocarbon synthetic oils and synthetic esters. Useful synthetic hydrocarbon oils include liquid polymers of alpha-olefins having the proper viscosity. Especially useful are the hydrogenated liquid oligomers of C₆ to C₁₂ alpha-olefins such as 1-decene trimer. Likewise, alkyl benzenes of proper viscosity such as didodecyl benzene, can be used. Useful synthetic esters include the esters of both monocarboxylic acid and polycarboxylic acids as well as monohydroxy alkanols and polyols. Typical examples are didodecyl adipate, pentaerythritol tetracaprate, di-2-ethylhexyl adipate, dilaurylsebacate and the like. Complex esters prepared from mixtures of mono and dicarboxylic acid and mono and dihydroxy alkanols can also be used.

Blends of hydrocarbon oils with synthetic oils are also useful. For example, blends of 10 to 25 weight percent hydrogenated 1-decene trimer with 75 to 90 weight percent 150 SUS (100°F) mineral oil gives an excellent lubricating oil base.

Other additives which may be present in the formulation include rust inhibitors, foam inhibitors, corrosion inhibitors, metal deactivators, pour point depressants, antioxidants, and a variety of other well-known additives.

The following examples illustrate the invention.

Example 1 (Preparative)

Preparation of a C₁₈-C₃₀ Alkylphenol

To a 2-liter flask, equipped with stirrer, Dean Stark trap, condensor and nitrogen inlet and outlet was added 857 gms of a predominantly C₁₈ to C₃₀ olefin mixture (olefin content: C₁₆-0.5%; C₁₈-6.6%; C₂₀-26.2%; C₂₂-27.7%; C₂₄-18.2%; C₂₆-9.0%; C₂₈-4.5%; C₃₀-28%; greater than C₃₀-4.5%) wherein the entire olefin fraction, at least 30 mole percent of said olefins contain trisubstituted vinyl groups (available from Ethyl Corporation, Baton Rouge, LA), 720 gms phenol, 55 gms of a sulfonic acid cation exchange resin (polystyrene crosslinked with divinylbenzene) catalyst (Amberlyst 15® available from Rohm and Haas, Philadelphia, Pennsylvania). The reaction mixture was heated to about 145°C for about 6 hours with stirring under a nitrogen atmosphere. The reaction mixture was stripped by heating under vacuum and the resulting product filtered hot over diatomaceous earth to afford 947 gms of a C₁₈-C₃₀ alkylphenol with a hydroxyl number of 118 and 56% para-alkylphenol content.

Example 2 (Preparative)

Preparation of a C₂₀-C₂₈ Alkylphenol

To a 2-liter flask, equipped with stirrer, Dean Stark trap, condensor and nitrogen inlet and outlet was added 674 gms of a predominantly C₂₀ to C₂₈ olefin mixture (olefin content: C₁₈-2%; C₂₀-28%; C₂₂-19%; C₂₄-13%; C₂₆-21%; C₂₈-11%; and greater than C₃₀-6%) wherein in the entire olefin fraction at least 20 mole percent of said olefins contain vinylidene groups (C₂₀-C₂₄ olefins and C₂₄-C₂₈ olefins are available from Chevron Chemical Company, San Francisco, CA and are then physically mixed at an equal mole basis to provide a C₂₀-C₂₈ olefin mixture), 211.5 grams of phenol, 43 grams of a sulfonic acid cation exchange resin (polystyrene crosslinked with divinylbenzene) catalyst (Amberlyst 15® available from Rohm and Haas, Philadelphia, PA). The reaction mixture was heated to about 140°C for about 8 hours with stirring under a nitrogen

atmosphere. The reaction mixture was stripped by heating under vacuum and the product was filtered hot over diatomaceous earth to afford 574 grams of a C₂₀-C₂₈ alkylphenol with a hydroxyl number of 110 and with 56% para-alkylphenol content.

5 *Example 3 (Preparative)* 5

Preparation of Tetrapropenylphenol

To a 2-liter flask, equipped with stirrer, Dean-Stark trap, condensor, and nitrogen inlet and outlet was added 567 grams of tetrapropylene, 540 grams of phenol, 72 grams of a sulfonic acid cation exchange resin (polystyrene crosslinked with divinylbenzene) catalyst (Amberlyst 15® available from Rohm and Haas, Philadelphia, PA). The reaction mixture was heated to about 110°C for about 3 hours with stirring under a nitrogen atmosphere. The reaction mixture was stripped by heating under vacuum and the resulting product filtered hot over diatomaceous earth to afford 626 grams of tetrapropenylphenol and with a hydroxyl number of 205 and with 96% para-alkylphenol content. 10 15

15 *Example 4 (Preparative)* 15

Into a 0.5-liter 3-neck flask, equipped with stirrer, Dean-Stark trap, condensor, and nitrogen inlet and outlet was charged 100 grams of phenol. The system was heated to 55°C and then charged with 55 grams of C₂₄-C₂₈ olefin, available from Chevron Chemical Company, San Francisco, CA, and 12.5 grams of Filtrol-13, an acid activated clay available from Filtrol Corporation, Los Angeles, CA. Afterwards, 130.5 grams of C₁₈-C₃₀ olefin, available from Ethyl Corp., Baton Rouge, LA, was added over 1 hour while heating the system from between 135°C to 145°C. The reaction was stopped and filtered. The filtered produce was transferred to a clean flask, placed under vacuum (~50 mm Hg) and heated to 215°C with a small nitrogen sweep. The nitrogen was shut off and the vacuum (~50 mm Hg) continued at 215°C for 30 minutes to yield an alkylphenol having a hydroxyl number of 106. 20 25

Example 5 (Preparative)

Preparation of Calcium Overbased Hydrocarbyl Sulfonate

30 A. *Preparation of Sodium Hydrocarbyl Sulfonate* 30

Into a reaction vessel is charged 646 grams of feedstock (solvent refined 500N lubricating oil which is a mixture of alkyl aromatics, naphthenes and paraffins). At 75°F, 150.8 grams of oleum (~27.6% SO₃) is charged to the reaction vessel over a 10-minute addition period. The reaction temperature is allowed to rise—generally to about 100°F. Afterwards, 12.3 ml of water as well as 540 ml of Chevron 265 thinner, which is a mixture of aromatics, naphthenes and paraffins, is added to the system. The system is maintained at 150°F for 1 hour. At this time, 125 ml of an aqueous solution containing 25% by weight sodium hydroxide is added to the system. The reaction is maintained at 150°F for 1 hour. After settling, the aqueous layer is removed and the organic solution then is maintained for at least 1 hour. After this period, any additional aqueous layer which had settled out is also removed. The system is stripped at 350°F, atmospheric pressure with an air sweep to yield the sodium hydrocarbyl sulfonate which is purified as follows: The sodium hydrocarbyl sulfonate is dissolved in 330 ml of aqueous secondary butyl alcohol. 160 ml of an aqueous solution containing 4% by weight sodium chloride is added to the system. The system is heated to 150°F and maintained at 150°F for 2 hours. After settling, brine is removed. An additional 80 ml of an aqueous solution containing 4% by weight sodium chloride is added to the system. The system is heated to 150°F and maintained at 150°F for 1 hour. After settling, brine is removed. 220 ml of water is added to the system and the system heated to 150°F. The system is maintained at 150°F for 1 hour. Afterwards, water and unsulfonated oil layer is removed leaving the aqueous secondary butyl alcohol solution containing the sodium hydrocarbyl sulfonate. 35 40 45 50

B. *Preparation of Calcium Hydrocarbyl Sulfonate*

To the aqueous secondary butyl alcohol solution containing the sodium hydrocarbyl sulfonate, produced as in A above, is added 550 ml of a solution containing water, secondary butyl alcohol and calcium chloride (~10% CaCl₂). The system is heated to 150°F and is maintained at 150°F for 1 hour. After settling, brine is removed. 340 ml of water and 170 ml of an aqueous solution containing 40% by weight calcium chloride is added to the system. The system is heated to 150°F and is maintained at 150°F for at least 1 hour. After settling, brine is removed. 340 ml of water and 170 ml of an aqueous solution containing 40% by weight calcium chloride is added to the system. The system is heated to 150°F and is maintained at 150°F for at least 1 hour. After settling, brine is removed. 340 ml of water is added to the system. The system is heated to 150°F and is maintained at 150°F for 1 hour. After settling, the aqueous layer is removed. An additional 340 ml of water is then added to the system. The system is heated to 150°F and is maintained at 150°F for 1 hour. After settling, the aqueous layer is removed. The aqueous secondary butyl alcohol solution is then stripped at elevated temperatures and reduced pressures 55 60 65

to yield calcium hydrocarbyl sulfonate.

C. Preparation of Calcium Overbased Hydrocarbyl Sulfonate

Into a 500-ml 3-neck round bottom flask equipped with a mechanical stirrer, is added sufficient diluent oil to the calcium hydrocarbyl sulfonate, produced above, to yield 270 grams of a composition at 1.65% by weight calcium. 42.4 grams water and 10.8 grams calcium hydroxide are added to the system. A reflux condenser is attached to one side neck and a thermometer is attached to the other side neck of the 3-neck round bottom flask. The system is heated to reflux (~210°F) and held there for at least 1 hour. The reaction system is then distilled by heating to a bottoms temperature of 330°F/atmospheric pressure. Afterwards, the temperature is raised to 400°F under vacuum (~20 mm Hg). The system is then cooled to 300°F and the vacuum is discontinued. 20 grams of diatomaceous earth is added to the product and the product filtered through a 1/4-inch diatomaceous earth pad on a Buchner funnel which is preheated prior to filtration to yield the title compound which is generally of approximately 16 Total Base Number.

Example 6

Preparation of 340 TBN Calcium Overbased Sulfurized Alkylphenol

Into a 2-liter, 4-neck flask was charged 196 grams of tetrapropenylphenol, prepared in a manner similar to Example 3, 354 grams of C₁₈-C₃₀ alkylphenol, prepared in a manner similar to Example 1, 410 grams of decyl alcohol, 20 grams of zinc di-(2-ethylhexyl) dithiophosphate, 40 grams of a calcium overbased hydrocarbyl sulfonate, prepared in a manner similar to Example 5 and 200 grams of Cit-Con 100N oil. The system was heated with agitation at 90°C at which time 296 grams of Ca(OH)₂ and 108 grams of sulfur were charged to the reaction system. The reaction system was then held at 90°C for 45 minutes. Afterwards, the reaction temperature was raised over a 15-minute period to 150°C whereupon 206 grams ethylene glycol was added over a 60-minute period via an addition funnel. After complete addition of ethylene glycol, the reaction temperature was increased to 160°C over a 15-minute period and held at this temperature for 1 hour. At this time, the stirring rate of the reaction mixture was increased to moderately fast, and the reaction temperature was then increased at a rate of 5°C per 20 minutes until the reaction temperature reached 175°C whereupon 144 grams of carbon dioxide was charged through a flowmeter to the reaction system over a 3-hour period. The reaction temperature was then increased to 195°C and the system stripped under vacuum (~10 mm of Hg) for a period of 30 minutes to yield 1269 grams of product which was purified by addition of 3 weight percent diatomaceous earth consisting of 50% Hi-Flo, and 50% of 512 Celite, commercial diatomaceous earth products available from Manville, Filtration and Minerals Division, Denver, CO, followed by filtration through a 1/4-inch Celite pad on a Buchner funnel. The resulting product has a Total Base Number of 340 (324 on second titrimeter); a viscosity of 720 centistokes at 100°C; a sulfur content of 4.4 weight percent; and a calcium content of 12.3 weight percent.

Example 7

Preparation of a 343 TBN Calcium Overbased Sulfurized Alkylphenol

Into a 10-gallon stainless steel reactor was charged 3.53 kilograms of tetrapropenylphenol, prepared in a manner similar to Example 3, 6.73 kilograms of C₁₈-C₃₀ alkylphenol, prepared in a manner similar to Example 1, 7.6 kilograms of decyl alcohol, 380 grams of zinc di-(2-ethylhexyl) dithiophosphate, 760 grams of a calcium overbased hydrocarbyl sulfonate, prepared in a manner similar to Example 5 and 3.8 kilograms of Cit-Con 100N oil. The system was heated with agitation to 90°C at which time 5.62 kilograms of Ca(OH)₂ and 2.05 kilograms sulfur were charged to the reaction system. The reaction system was then held at 90°C for 45 minutes. Afterwards, the reaction temperature was raised over a 15-minute period to 150°C whereupon 3.91 kilograms ethylene glycol was added over a 60-minute period via an addition flask. After complete addition of ethylene glycol, the reaction temperature was increased to 160°C and held at this temperature for 1 hour. At this time, the stirring rate of the reaction mixture was increased and the reaction temperature was then increased at a rate of 5°C per 20 minutes until the reaction temperature reached 175°C whereupon 2.74 kilograms of CO₂ was charged to the reaction system over a 3-hour period. The reaction temperature was then increased to 195°C and the system stripped under vacuum (~10 mm of Hg) for a period of 30 minutes. The system was cooled overnight and then heated and agitated. The product was then purified by addition of 3 weight percent diatomaceous earth consisting of 50% Hi-Flo, and 50% of 512 Celite, commercial diatomaceous earth products available from Manville, Filtration and Minerals Division, Denver, CO, followed by filtration to yield a product having a Total Base Number of 343 (324 on second titrimeter); a viscosity of 463 centistokes at 100°C; a sulfur content of 4.4 weight percent, a calcium content of 12.4 weight percent and 1.6% crude sediment.

Example 8

Into a 1-liter, 4-neck flask was added 99 grams of tetrapropenylphenol, prepared in a manner similar to Example 3, 167 grams of a C₂₀-C₂₈ alkylphenol, prepared in a manner similar to Example 2, 210 grams of decyl alcohol, 10 grams of zinc di-(2-ethylhexyl) dithiophosphate, 20 grams of a calcium overbased hydrocarbyl sulfonate, prepared in a manner similar to Example 5 and 100 grams of Cit-Con 100N oil. The system was heated with agitation to 90°C at which time 148 grams of Ca(OH)₂ and 56 grams of sublimed sulfur were charged to the reaction system. The reaction was then held at 90°C for 45 minutes. Afterwards, the reaction temperature was raised over a 15-minute period to 150°C whereupon 103 grams of ethylene glycol was added over a 60-minute period. After complete addition of the ethylene glycol, the reaction temperature was increased to 160°C and held at this temperature for 1 hour. At this time, the reaction temperature was increased at a rate of 5°C per 20 minutes until the reaction temperature reached 175°C whereupon 72 grams of carbon dioxide was charged to the reaction system over a 3-hour period. The reaction temperature was then increased to 195°C and the system stripped under vacuum (~10 mm Hg) for a period of 30 minutes. Sediment was removed and 800 ml of 250 thinner which is a mixture of aromatics, paraffins and naphthenes was added to the system as well as 3 weight percent diatomaceous earth consisting of 50% Hi-Flo and 50% of 512 Celite, commercial diatomaceous earth products available from Manville, Filtration and Minerals Division, Denver, CO. The system was filtered through a 1/4-inch Celite pad on a Buchner funnel. Afterwards, the thinner was removed by stripping at elevated temperatures and reduced pressures to yield 581 grams of a calcium overbased sulfurized alkylphenol having a Total Base Number of 328 (obtained from second titrimeter) a viscosity of 365 centistokes at 100°C; a sulfur content of 3.96 weight percent; and a calcium content of 12.3 weight percent.

Example 9

Into a 2-liter, 4-neck flask was added 99 grams of tetrapropenylphenol, prepared in a manner similar to Example 3, 167 grams of a C₂₀-C₂₈ alkylphenol, prepared in a manner similar to Example 2, 210 grams of decyl alcohol, 10 grams of zinc di-(2-ethylhexyl) dithiophosphate, 20 grams of calcium overbased hydrocarbyl sulfonate, prepared in a manner similar to Example 5 and 100 grams of Cit-Con 100N oil. The system was heated with agitation to 90°C at which time 138 grams of calcined Dolomite, Ca(OH)₂.Mg(OH)₂, and 56 grams of sublimed sulfur were charged to the reaction system. The reaction was then held at 90°C for 45 minutes. Afterwards, the reaction temperature was raised over a 15-minute period to 150°C whereupon 103 grams of ethylene glycol was added over a 60-minute period. After complete addition of the ethylene glycol, the reaction temperature was increased to 160°C and held at this temperature for 1 hour. At this time, the reaction temperature was increased at a rate of 5°C per 20 minutes until the reaction temperature reached 175°C whereupon 74 grams of carbon dioxide was charged to the reaction system over a 3-hour period. The reaction temperature was then raised to 195°C and the system stripped under vacuum (~10 mm Hg) for a period of 30 minutes. Sediment was removed and 800 ml of Chevron 250 thinner, which is a mixture of aromatics, paraffins and naphthenes was added to the system as well as 3 weight percent diatomaceous earth consisting of 50% Hi-Flo and 50% 512 Celite, which are commercial diatomaceous earth products available from Manville, Filtration and Minerals Division, Denver, CO. The system was filtered through a 1/4-inch Celite pad on a Buchner funnel. Afterwards, the thinner was removed by stripping at elevated temperatures and reduced pressures to yield 280 grams of a calcium-magnesium overbased sulfurized alkylphenol having a Total Base Number of 294 (obtained from second titrimeter); a viscosity of 154 centistokes at 100°C; a sulfur content of 3.65 weight percent; a calcium content of 7.62 weight percent; and a magnesium content of 2.14 weight percent.

Example 10

Into a 1-liter, 3-neck flask was added 104 grams of tetrapropenylphenol, prepared in a manner similar to Example 3, 187 grams of a mixture of C₁₈-C₃₀ and C₂₄-C₂₈ alkylphenol, prepared in a manner similar to Example 4, 105 grams of decyl alcohol, 10 grams of zinc di-(2-ethylhexyl) dithiophosphate, 20 grams of calcium overbased hydrocarbyl sulfonate, prepared in a manner similar to Example 5, and 100 grams of Cit-Con 100N oil. The system was heated with agitation to 90°C at which time 148 grams of Ca(OH)₂ and 56 grams of sublimed sulfur were charged to the reaction system. The reaction was then held at 90°C for 45 minutes. Afterwards, the reaction temperature was raised over a 15-minute period to 150°C whereupon 103 grams of ethylene glycol was added over a 60-minute period. After complete addition of the ethylene glycol, the reaction temperature was increased to 160°C and held at this temperature for 1 hour. At this time, the reaction temperature was increased at a rate of 5°C per 20 minutes until the reaction temperature reached 175°C whereupon 72 grams of carbon dioxide was charged to the reaction system over a 3-hour period. The reaction temperature was then raised to 195°C and the system stripped under vacuum (~10 mm Hg) for a period of 30 minutes. Sediment was removed and 800 ml of Chevron 250 thinner, which is a mixture of aromatics, paraffins and

naphthenes, was added to the system as well as 3 weight percent diatomaceous earth consisting of 50% of Hi-Flo and 50% 512 Celite, which are commercial diatomaceous earth products available from Manville, Filtration and Minerals Division, Denver, CO. The system was filtered through a 1/4-inch Celite pad on a Buchner funnel. Afterwards, the thinner was removed by stripping at elevated temperatures and reduced pressures to yield 601 grams of a calcium overbased sulfurized alkylphenol having a Total Base Number of 349 (324 TBN on second titrimeter), a viscosity of 441 centistokes at 100°C; a sulfur content of 4.27 weight percent; and a calcium content of 12.4 weight percent. 5

10 Example 11 10

Into a 1-liter, 3-neck flask was added 102 grams of tetrapropenylphenol, prepared in a manner similar to Example 3, 187 grams of a mixture of C₁₈-C₃₀ and C₂₄-C₂₈ alkylphenol, prepared in a manner similar to Example 4, 105 grams of decyl alcohol, 20 grams of zinc di-(2-ethylhexyl) dithiophosphate, 20 grams of a polyisobutenyl succinimide dispersant composition [prepared by reacting 1 mole of polyisobutenyl succinic anhydride, where the polyisobutenyl group has a number average molecular weight of about 950, with 0.87 mole of tetraethylenepentaamine; then diluting to about 50% actives with diluent oil—contains 2.1% nitrogen] and 100 grams of Cit-Con 100N oil. The system was heated with agitation to 90°C at which time 148 grams of Ca(OH)₂ and 56 grams of sublimed sulfur were charged to the reaction system. The reaction was then held at 90°C for 45 minutes. Afterwards, the reaction temperature was raised over a 15-minute period to 150°C whereupon 103 grams of ethylene glycol was added over a 60-minute period. After complete addition of the ethylene glycol, the reaction temperature was increased to 160°C and held at this temperature for 1 hour. At this time, the reaction temperature was increased at a rate of 5°C per 20 minutes until the reaction temperature reached 175°C whereupon 72 grams of carbon dioxide was charged to the reaction system over a 3-hour period. The reaction temperature was then raised to 195°C and the system stripped under vacuum (~10 mm Hg) for a period of 30 minutes. Sediment was removed and 800 ml. of Chevron 250 thinner which is a mixture of aromatics, paraffins and naphthenes, was added to the system as well as 3 weight percent diatomaceous earth consisting of 50% of Hi-Flo and 50% Celite, which are commercial diatomaceous earth products available from Manville, Filtration and Minerals Division, Denver, CO. The system was filtered through a 1/4 inch Celite pad on a Buchner funnel. Afterwards, the thinner was removed by stripping at elevated temperatures and reduced pressures to yield a calcium overbased sulfurized alkylphenol having a Total Base Number of 352 (obtained from first titrimeter); a viscosity of 893 centistokes at 100°C; a sulfur content of 4.02 weight percent; and a calcium content of 11.3 weight percent. 15 20 25 30 35

EXAMPLE 12

Into a 2-liter, 4-neck flask was charged 99 grams of tetrapropenylphenol prepared in a manner similar to Example 3, 192 grams of C₂₀-C₂₈ alkylphenol prepared in a manner similar to Example 2, 210 grams of decyl alcohol, 10 grams of 2-mercaptobenzothiazole, 20 grams of a calcium overbased hydrocarbyl sulfonate prepared in a manner similar to Example 5, and 100 grams of Cit-Con 100N oil. The system was heated with agitation at 90°C at which time 148 grams of Ca(OH)₂ and 49 grams of sulfur were charged to the reaction system. The reaction system was then held at 90°C for 45 minutes. Afterwards, the reaction temperature was raised over a 15-minute period to 150°C whereupon 93 grams of ethylene glycol was added dropwise over a 60-minute period via a constant addition funnel. After complete addition of ethylene glycol, the reaction temperature was increased to 160°C over a 15-minute period and held at this temperature for 1 hour. The reaction mixture was then increased to 170°C over a 15-minute period and held at that temperature for 1 hour. The reaction temperature was then raised to 175°C over a 10-minute period. At this time, 72 grams of carbon dioxide were charged through a flowmeter to the reaction system over a 3-hour period. The reaction mixture was stirred for a 10-minute period and then sparged for a 10-minute period with N₂. The reaction temperature was increased to 185°C and the system was stripped under vacuum (~0.5 mm. of Hg) for a period of 40 minutes to yield 622 grams of crude product. About 1 liter of 250 Thinner which is a mixture of aromatics, paraffins and naphthenes was added to the system as well as 3 wt % diatomaceous earth consisting of 50% Hi-Flo and 50% Celite, commercial diatomaceous earth products available from Manville, Filtration and Minerals Division, Denver Co. The system was filtered through a 1/4-inch Celite pad on a Buchner funnel. Afterwards, the thinner was removed by stripping at elevated temperatures and reduced pressures (about 95°C, 3 cm Hg) to yield 434 grams of a calcium overbased sulfurized alkylphenol having a Total Base Number 294 (second titrimeter); a viscosity of 116 centistokes at 100°C; a sulfur content of 3.91%; and a calcium content of 10.8%. The crude sediment was found to be 5.2%. 40 45 50 55 60

EXAMPLE 13

65 Into a 1-liter, 4-neck flask was charged 99 grams of tetrapropenylphenol prepared in a manner 65

similar to Example 3, 167 grams of C₂₀-C₂₈ alkylphenol prepared in a manner similar to Example 2, 105 grams decyl alcohol, 10 grams of 2-mercaptobenzothiazole, 20 grams of a calcium overbased hydrocarbyl sulfonate prepared in a manner similar to Example 5, and 100 grams of Cit-Con 100N oil. The system was heated with agitation at 90°C at which time 148 grams Ca(OH)₂ and 56 grams sublimed sulfur were charged to the reaction system. The reaction system was then held at 90°C for 45 minutes. Afterwards, the reaction temperature was raised over a 15-minute period to 150°C whereupon 103 grams ethylene glycol was added over a 60-minute period via a constant addition funnel. After complete addition of ethylene glycol, the reaction temperature was increased to 160°C over a 15-minute period and held at this temperature for 1 hour. At this time, the stirring rate of the reaction mixture was increased to moderately fast, and the reaction mixture was increased at a rate of 5°C per 20 minutes until the reaction temperature reached 175°C whereupon 72 grams carbon dioxide was charged through a flowmeter to the reaction system over a 3-hour period. The reaction temperature was then increased to 195°C and the system stripped under vacuum (~10 mm of Hg) for a period of 30 minutes to yield 626 grams of product. A sample for sediment determination was removed; then 800 ml of 250 Thinner which is a mixture of aromatics, paraffins and naphthenes was added to the system as well as 3 wt % diatomaceous earth consisting of 50% Hi-Flo and 50% 512 Celite, commercial diatomaceous earth products available from Manville, Filtration and Minerals Division, Denver, Co. The system was filtered through a 1/4-inch Celite pad on a Buchner funnel. Afterwards, the thinner was removed by stripping at elevated temperatures and reduced pressures (150°C, ~5 mm Hg) to yield 557 grams of a calcium overbased sulfurized alkylphenol having a Total Base Number of 323; a viscosity of 1.186 centistokes at 100°C; a sulfur content of 4.19 wt %; and a calcium content of 12.7 wt %. The crude sediment was found to be 2.0%.

EXAMPLE 14

Into a 2-liter, 4-neck flask was added 99 grams of tetrapropenylphenol prepared in a manner similar to Example 3, 192 grams of C₂₀-C₂₈ alkylphenol prepared in a manner similar to Example 2, 210 grams decyl alcohol, 10 grams of ORTHORIX, a commercially available calcium polysulfide product sold by Chevron Chemical Company, San Francisco, CA, 20 grams of a calcium overbased hydrocarbyl sulfonate prepared in a manner similar to Example 5, and 100 grams of Cit-Con 100N oil. The system was heated with agitation to 90°C at which time 148 grams Ca(OH)₂ and 56 grams sublimed sulfur were charged to the reaction system. The reaction system was then held at 90°C for 45 minutes. Afterwards, the reaction temperature was raised over a 15-minute period to 150°C whereupon 103 grams ethylene glycol was added over a 60-minute period. After complete addition of ethylene glycol, the reaction temperature was increased to 160°C and held at this temperature for 1 hour. At this time, the reaction temperature was increased at a rate of 5°C per 20 minutes until the reaction temperature reached 175°C whereupon 72 grams carbon dioxide was charged to the reaction system over a 3-hour period. The reaction temperature was then increased to 195°C and the system stripped under vacuum (~10 mm of Hg) for a period of 30 minutes. A sample for sediment determination was removed; then 800 ml of 250 Thinner which is a mixture of aromatics, paraffins and naphthenes was added to the system as well as 3 wt % diatomaceous earth consisting of 50% Hi-Flo and 50% 512 Celite, both commercial diatomaceous earth products available from Manville, Filtration and Minerals Division, Denver, Co. The system was filtered through a 1/4-inch Celite pad on a Buchner funnel. Afterwards, the thinner was removed by stripping at elevated temperatures and reduced pressures to yield 547 grams of a calcium overbased sulfurized alkylphenol having a Total Base Number of 294; a viscosity of 471 centistokes at 100°C; a sulfur content of 3.39 wt %; and a calcium content of 11.1 wt %. The crude sediment was found to be 4.0%.

CLAIMS

1. A method of preparing a Group II metal overbased sulfurized alkylphenol which comprises the steps of:
 - (a) introducing into an inert hydrocarbon diluent an alkylphenol in which the alkyl group contains a sufficient number of carbon atoms to render oil-soluble the resulting Group II metal overbased sulfurized alkylphenol, an oil-soluble Group II metal overbased natural or synthetic hydrocarbyl sulfonate, a sulfurization catalyst, and a higher alkanol of at least 8 carbon atoms; the oil-soluble Group II metal overbased natural or synthetic hydrocarbyl sulfonate being employed at from 1 to 20 weight percent to the alkylphenol; the sulfurization catalyst being employed at from 0.5 to 10 weight percent to the alkylphenol, and the higher alkanol being employed at a molar ratio to the alkylphenol of from 0.5 to 5;
 - (b) heating the resulting reaction system to a temperature of from 90°C to 155°C;
 - (c) introducing into the reaction system a Group II metal oxide, hydroxide or C₁-C₈ alkoxide and sulfur at a temperature sufficient to effect sulfurization of the alkylphenol followed by addition at from 145°C to 165°C of a C₂-C₄ alkylene glycol; the Group II metal oxide, hydroxide

or C₁-C₆ alkoxide being employed at a molar ratio to the alkylphenol of from 1 to 4, the sulfur being employed at a molar ratio to the alkylphenol of from 1.5 to 4, and the C₂-C₄ alkylene glycol being employed at a molar ratio to the alkylphenol of from 1 to 4;

- (d) heating the resulting reaction system at a temperature sufficient to effect removal of a
5 portion of the water in the system; 5
- (e) heating the system to a temperature of from 160°C to 190°C;
- (f) introducing into the reaction system carbon dioxide, the carbon dioxide being employed at a molar charge to the alkylphenol of from 1 to 3; and
- (g) heating the system under reduced pressure at a temperature and pressure sufficient to
10 remove from the system a portion of the water, C₂-C₄ alkylene glycol and the alkanol of at least 10
8 carbon atoms, and any unreacted carbon dioxide, and thereafter recovering the required Group
II metal overbased sulfurized alkylphenol from the reaction system.
2. A method according to Claim 1, wherein the alkyl group of said alkylphenol contains from
25 to 100 mole percent predominantly straight-chain alkyl groups of from 15 to 35 carbon
15 atoms and wherein from 75 to 0 mole percent of the alkyl groups are polypropenyl of from 9 to 15
18 carbon atoms.
3. A method according to Claim 1 or 2, wherein said higher alkanol is decyl alcohol and said
C₂-C₄ alkylene glycol is ethylene glycol.
4. A method according to Claim 1, 2 or 3, wherein the Group II metal in said Group II metal
20 oxide, hydroxide or C₁-C₆ alkoxide is calcium, barium or magnesium. 20
5. A method according to Claim 4, wherein the Group II metal is calcium.
6. A method according to Claim 4, wherein the Group II metal hydroxide is Dolomite (Ca(OH)₂
Mg(OH)₂).
7. A method according to any preceding claim, wherein the sulfurization catalyst is a zinc
25 dihydrocarbyl dithiophosphate wherein each hydrocarbyl is independently selected such that the 25
dihydrocarbyl group contains from 6 to 30 carbon atoms.
8. A method according to Claim 7, wherein the sulfurization catalyst is zinc di-(2-ethylhexyl)
dithiophosphate.
9. A method of preparing a Group II metal overbased sulfurized alkylphenol, substantially as
30 described in any one of the foregoing Examples 6 to 14. 30